University of Alberta Library
0 1620 3416667 6

For Reference

NOT TO BE TAKEN FROM THIS ROOM

# BASE EXCHANGE STUDIES OF SOME SOLONETZIC SOILS OF THE PEACE RIVER DISTRICT.

A. Wynnyk,

University of Alberta.

April 1950.

Thesis
1950
#52

For Reference

NOT TO BE TAKEN FROM THIS ROOM

Ex libris
universitatis
albertaensis

UNIVERSITY OF ALBERTA
QUAECUMQUE VERA

Digitized by the Internet Archive
in 2018 with funding from
University of Alberta Libraries

https://archive.org/details/baseexchangestud00wynn

THE UNIVERSITY OF ALBERTA

# BASE EXCHANGE STUDIES OF SOME SOLONETZIC SOILS OF THE PEACE RIVER DISTRICT

A DISSERTATION

SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES

IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF SCIENCE.

FACULTY OF AGRICULTURE

by

ANDREW WYNNYK

EDMONTON, ALBERTA.

APRIL, 1950.

TABLE OF CONTENTS

Page

INTRODUCTION..... 1

REVIEW OF LITERATURE

Base Exchange Determination..... 2

Characteristics of North American Solonetz Soils..... 7

PURPOSE AND OUTLINE OF INVESTIGATION..... 9

SAMPLING AND DESCRIPTION OF PROFILES..... 9

ANALYTICAL METHODS.

Preparing of Sample..... 14

Methods of Extracting..... 15

Ammonium Acetate Extracting Solution..... 16

Extracting Procedure..... 16

Total Exchange Capacity..... 17

Determining Exchangeable Hydrogen..... 18

Preparation of Extract for Analysis of Bases..... 20

Determining Sulphate..... 21

Calcium and Magnesium Determination..... 21

Determining pH of Soil..... 22

Water Soluble Solids..... 22

Flame Photometer Method of Determining Exchangeable Potassium..... 23-32

Determining Exchangeable Sodium with Flame Photometer..... 33-38

RESULTS..... 38-47

DISCUSSION OF RESULTS.

Profile 1..... 48

Page

DISCUSSION OF RESULTS (cont'd.)

Profile 2..... 49

Profile 3..... 49

General Discussion..... 50

SUMMARY..... 51

ACKNOWLEDGEMENT..... 52

BIBLIOGRAPHY..... 53

## LIST OF TABLES AND FIGURES


Page

Figure 1. Graph showing the increase in pH of 500 ml. 1 N ammonium acetate with the addition of $H^+$ as .2N acetic acid ..... 18

Table 1. Effect of exchangeable Ca and Na on the pH of 1 N ammonium acetate ..... 20

Figure 2. Graphs showing the effects of additions of calcium, magnesium, or sodium on percentage transmission of a potassium solution as measured by flame photometer.. 27

Table 2. Variation in amounts of potassium found in a soil extract due to the kind of standard used ..... 30

Table 3. Amounts of potassium added to a soil extract and corresponding amounts of potassium found by using a flame photometer method of determination ..... 32

Figure 3. Graphs showing the effects of addition of calcium, magnesium, and potassium on percentage transmission of a sodium solution as measured by flame photometer .... 34

Table 4. Amounts of sodium added to a soil extract and the corresponding amounts of sodium found by using a flame photometer method of determination ..... 38

Table 5. Profile 1 from Valleyview. Amounts of cations extracted with 1 N ammonium acetate, water soluble solids, exchange capacity, and pH ..... 40

Table 5A. Profile 1 from Valleyview. Percentage of cations extracted from the various horizons with 1 N ammonium acetate ..... 41

Table 6. Profile 2 from east of Clairmont. Amounts of cations extracted with 1 N ammonium acetate, water soluble solids, exchange capacity, and pH ..... 42

Table 6A. Profile 2 from east of Clairmont. Percentage of cations extracted from the various horizons with 1 N ammonium acetate. 43

Page

Table 7. Profile 3 from Buffalo Lake. Amounts of cations extracted with 1 N ammonium acetate, water soluble solids, exchange capacity, and pH ..... 44

Table 7A. Profile 3 from Buffalo Lake. Percentage of cations extracted from the various horizons with 1 N ammonium acetate .. 45

Table 8. Comparison of profiles with average (of 6) for the Black Zone ..... 46

# INTRODUCTION

Solonetz soils were first described and classified in Russia (9). Soon they became associated in the literature with an arid or semi-arid climate and prairie vegetation. Studies in Russia revealed that the solonetz soils there were high in exchangeable sodium and Gedroiz advanced a theory associating the high sodium content with the characteristic physical and morphological properties. The high content of exchangeable sodium was believed to be the cause of a highly dispersed phase of soil colloids which under proper climatic conditions would result in the development of the hard, compact columns characteristic of solonetzic soil B horizons.

Studies in North America have shown that there are large areas of morphologically similar soils on this continent. Their frequent occurrence throughout prairie regions strengthened the observed association of these soils with a dry climate. However, studies of the chemical properties of these soils revealed considerable differences from the solonetz first described in Russia. In general the solonetz on this continent are lower in exchangeable sodium content. Some solonetz (11,25,35) are reported to be relatively high in magnesium. With more extensive studies in North America, there have been reported probably more exceptions than conformaties to the original idea of the chemistry of solonetzic soils. For this reason there appears to be a growing tendency in the classification of these soils to lay greater emphasis on the mor-

phological features which are their more consistent characteristics.

"Solonetzic areas" in Alberta (28) are estimated to cover over seven million acres. The work of MacGregor and Wyatt (22) deals with soils from some of these areas but their work though extensive does not include the Peace River Area. The occurrence of solonetz in the Peace River District is of particular interest in that the area is in a different climatic and zonal region than is generally associated with solonetzic soils.

## REVIEW OF LITERATURE

### Base Exchange Determinations.

The nature of the exchangeable ions influence some of the physical properties of soil colloids. Since solonetz soils differ from the zonal soils by their striking morphological and physical features, which are attributed to the nature of their exchangeable ions, studies of these intrazonal soils is closely associated with base exchange studies.

The underlying theory of base exchange study is that a soil contains numerous particles of clay minerals around which are adsorbed varying amounts and kinds of cations. The adsorption of these cations is not permanent. These cations are replaceable or exchangeable and their proportions vary widely in different fields of soils and also in the different horizons of a particular soil profile. Many of the physical

and chemical characteristics of soils are determined by the amounts and nature of adsorbed cations. Base exchange studies are made by displacing these adsorbed cations from the exchange complex of the soil. This may be accomplished by electrodialysis (23,30) or more commonly by leaching with an extracting solution. Theoretically the amount of cations released by a solution should be equal to the cations absorbed from the extracting solution. The total capacity of a soil to hold absorbed cations is known as its base exchange capacity.

Extracting solutions that have been used for base exchange studies may be grouped as follows:

(1) neutral unbuffered salts.

(2) neutral buffered salts.

(3) hydrolyzed salts (buffered).

(4) weak and dilute acids.

These various types of extracting solutions for base exchange work have enjoyed varying popularity. In determining base exchange capacity Puri (31,32) first recommended neutral unbuffered salts because the extracting solution immediately takes on the pH of the soil and supposedly leaves the soil with the same degree of saturation. This idea was not widely accepted and buffered solutions were soon preferred. Several workers (13,24,37) have recently used buffered barium chloride for extracting exchangeable bases. The main disadvantage of this extracting solution is that it is not very suitable for deter-

mining the total exchange capacity. Total exchange capacity has to be determined on another sample of the same soil using a different solution. In recent years dilute acids have not been used commonly in base exchange work because of their great dissolving action. Thus besides replacing the exchangeable cations, acids will release bases from substances not involved in the replacement reaction.

The most widely used extracting solution is ammonium acetate, which is strongly buffered. Schollenberger and Dreibelbis (37) list the following advantages of ammonium acetate as a leaching agent in base exchange work.

(1) It is strongly buffered at a pH of 7.

(2) The same samples can be used for determination of base exchange capacity and total exchangeable bases.

(3) It can easily be expelled by evaporation.

(4) It is soluble in alcohol and any excess can be washed out of the soil before determining total exchange capacity.

(5) It is inexpensive and can be obtained in a relatively pure form.

To the above list the following additional advantages may be added:

(6) It is widely used and affords a better

basis for comparisons with results of other workers.

(7) It is possible to determine exchangeable hydrogen on the same extract.

Base exchange studies of solonetzic soils are considerably more complicated than similar studies of normal soils because of the frequent presence of salts or alkali. Saline soils contain bases not only in the exchange complex but also as free salts. The writer knows of no practical way by which it is possible to determine the amounts of the bases coming from the exchange complex and the amounts coming from the salts in the soil. Washing out the soluble salts with distilled water has been the most commonly used method for attempting to separate the bases present as salts from those in the exchange complex. In a saline soil, we assume that a temporary equilibrium is approached between the exchangeable bases adsorbed on the micelle, the soil solution, and the solid phase of the soil salts. Washing out the salts is certain to affect this equilibrium. The solubilities of the salts differ and some salts will be removed much more readily than others.

For example suppose that a soil sample containing sodium sulphate and calcium sulphate is to be leached with $CO_2$ free water to remove the salts prior to the determination of exchangeable cations. Assuming that the common

laws of chemistry apply and that the soil has reached an equilibrium, we would expect that most of the Ca will be in the form of calcium sulphate, the least soluble form. Any excess of the sulphate will be as sodium sulphate. Taking into account the solubilities and common ion effects we can calculate the concentration of sodium and calcium in a soil solution saturated with respect to this salt combination. Initially the soil should be at equilibrium with a predominantly sodium solution. When this soil is leached with water to remove the soluble salts, sodium sulphate being much more soluble will soon be removed. Then gradually the calcium sulphate will dissolve. Following is an illustration of the change in kind and ratio of cation in a soil solution which might occur under these circumstances.

| | Conc. of Na | Conc. of Ca |
|---|---|---|
| Before leaching with water | 2.7 N | .000087 N |
| After all sodium sulphate is removed | Nil | .016 N |

Whereas at first the soil was in a predominantly sodium solution, in the later stage of the washing the soil is bathed in a calcium solution. Undoubtedly this would alter the base exchange characteristics of the soil.

Bentley (4) has definitely shown that exchangeable sodium is displaced by leaching with distilled water. The displacement will become much more effective when some of the calcium salts of the soil are brought into solution.

Procedures which involve leaching out the salts with distilled water will give an under-estimation of exchangeable sodium in the soil.

The base exchange reaction is reversible and relatively rapid. The exchange complex will be affected by the change in the surrounding solution. It is not assumed that the change in relative concentration is the only factor involved but it is one of them. Joffe and Zimmerman (17) leached soils with solutions containing different amounts of various cations. Their work shows that the ratio of cations adsorbed is affected by the ratio, combinations, and concentrations of the different cations in the leaching solutions.

Characteristics of North American Solonetz Soils.

Generally the solonetz soils on this continent that have been reported on are too low in sodium to compare with the sodium solonetz in Russia although their morphological characteristics appear to be the same. Neither do all the North American solonetz soils fit into the classification as given by de Sigmond (9) who states that a minimum of 12 - 15% (m.e. basis) of the exchangeable bases must be sodium for a development of a solonetz. The Oklahoma solonetz reported on by Murphy and Daniel (26) are probably the only solonetz that without exception meet de Sigmond's minimum.

In Alberta MacGregor and Wyatt (22) found that

calcium was the dominant ion in the exchange complex and magnesium was appreciably lower. The amount of sodium present was found to be considerably lower than calcium or magnesium. Of the 13 profiles analyzed from the Brown Soil Zone, MacGregor and Wyatt obtained an average of 7% (m.e. basis) exchangeable sodium and having a range of 1 - 16%. In the Black Soil Zone they found an average (of 6 profiles) of 12% exchangeable sodium and the range being 1 - 32%.

Mitchell and Riecken (25) reported that Saskatchewan solonetz contain relatively small proportions of exchangeable sodium. The presence of an excess of exchangeable magnesium over calcium in the $B_2$ horizon appeared to be typical of some solonetz in that province. Rost (35) reports similar features for the solonetz in Minnesota. Ellis and Caldwell (11) report "magnesium solonetz" in Manitoba.

Bentley and Rost (5) explain how weathering of a solonetz soil high in sodium may result, at a certain stage, in a soil containing relatively large amounts of exchangeable magnesium. This explanation does not contradict the original classical concept concerning the origin and development of solonetz soils. This explanation is related to Riecken's (33) report that at pH 8 or more the magnesium in a soil may tend to percipitate out and that there would be a tendency for the magnesium to accumulate in any horizons having this or a higher pH.

## PURPOSE AND OUTLINE OF INVESTIGATION.

The purpose of this investigation was to study solonetzic soils of the Peace River District and compare them with similar soils found elsewhere. Solonetz soils in this area are of special interest for two reasons:

(1) They occur in an area geographically remote from the solonetz studied by MacGregor and Wyatt (22).

(2) They occur in a generally wooded and fairly humid region, an environment different to that traditionally associated with solonetz soils.

This report is concerned with work done on three profiles taken in the fall of 1948. The locations of these profiles are given under the section on sampling and descriptions of profiles.

In doing the work reported it was necessary to use base exchange methods suitable for the soils concerned. It was also necessary to establish suitable methods for flame photometer determination of sodium and potassium in the extracts obtained.

## SAMPLING AND DESCRIPTION OF PROFILES.

The samples were collected in September, 1948. Three profiles were sampled in the southern part of the Peace River District. In as much as all three profiles

were taken south of the line from the Saddle Hills to the Birch Hills and to the Puskwaskau Hills, we can consider that these samples are from the same area.

The occurrence of these solonetz soils is in a generally wooded zone and the amount of precipitation would be similar to that of the Edmonton area (i.e. about 18 inches annually). However, in this solonetz area the immediately surrounding vegetation is not that of a wooded zone. Grass, shrubs, and clumps of poplar and willow is the typical cover. All three profiles were taken from a till area.

The profiles sampled are designated as Profile 1, 2 and 3, and are referred to in that way in this report.

Sampling was done according to the horizons that could be differentiated in the profile either by color, structure, texture, or materials found in the horizon. Air dry colors are given and the color designations are according to revised Munsell color chart used by the Soil Survey.

## PROFILE 1

Profile 1 was sampled in N.E. 15-70-20-W5, near Valleyview on a 1% slope of a crown of a hill.

Following is a description of Profile 1.

Depth in inches

| | | |
|---|---|---|
| 0 - 2 | $A_{11}$ | - Dark grayish brown loam with a very fine granular to powdery structure. pH 5.6. |

Profile 1 (continued.)

| Depth in inches | | |
|---|---|---|
| 2 - 5 | $A_{12}$ | - Light brownish gray loam with a ~~porous~~ somewhat platy structure. pH 5.3. |
| 5 - 6 | $A_2$ | - Light brownish gray fine sandy loam. Platy but breaks easily into small irregular fragments. pH 5.2. |
| 6 - 8 | $B_1$ | - Dark grayish brown clay to clay loam. This horizon includes the rounded tops of columns which break up into small blocky fragments. pH 5.0. |
| 8 - 13 | $B_{21}$ | - Dark grayish brown clay. The macrostructure is columnar, hard, and compact, and the mesostructure is blocky. Root-mats are found on intersurfaces. pH 6.1. |
| 13 - 20 | $B_{22}$ | - Dark grayish brown clay. Structure is similar to that of $B_{21}$ but the columns are slightly less pronounced and tend to break up into irregular clods. pH 7.5. |
| 20 - 30 | $B_{Ca}$ | - Light brownish gray clay speckled with lime and salt accumulation. The structure is small blocky and relatively friable. pH 7.4. |
| 30 - 36 | $B_{SO_4}$ | - Light gray clay with a blocky structure and salts accumulation. pH 7.3. |
| at 55" | C | - Light brownish gray clay. This parent material is till containing some stones and occasional coal flakes. It breaks up into small blocky fragments. pH 7.6. |
| at 4 ft. | Bedrock | - A light brownish gray sandstone which is quite variable with some iron stone and the occasional thin seam of peaty coal. pH 7.5. Sample was taken from an exposure about 200 ft. from where the soil profile was sampled. |

## PROFILE 2.

Profile 2 was sampled east of Clairmont in N.E. 12-72-4-W6. The sampling was in a valley but in a well drained position. A large hill is found about 3/4 mile west of where the soil was sampled.

Following is a description of Profile 2.

| Depth in inches | | |
|---|---|---|
| 0 - 2 | $A_1$ - | Dark grayish brown loam practically structureless. pH 5.5. |
| 2 - 4 | $A_2$ - | Light brownish gray very fine sandy loam. The structure is somewhat platy and the horizon is wavy and variable in thickness. pH 5.7. |
| 4 - 5 | $B_1$ - | Dark grayish brown clay to clay loam. This horizon consists of the rounded tops of the columns. pH 5.7. |
| 5 - 10 | $B_{21}$- | Dark grayish brown clay. This horizon consists of the upper portion of the hard, compact columns and breaks down into sharp angular blocky fragments. Root mats are found along cleavage faces. pH 6.1. |
| 10 - 15 | $B_{22}$- | Dark gray clay. There is a sharp stony contact with the horizon above. The material is more friable, darker and less matted than in the above horizon. pH 7.5. |

Profile 2 (continued.)

| Depth in inches | | |
|---|---|---|
| 15 - 21 | $B_{Ca}$ | - Dark grayish brown clay with a small blocky structure. pH 7.4. |
| 21 - 31 | $B_{SO_4}$ | - Light gray to light brownish gray clay with accumulation of salts. pH 7.4. |
| 31 - 38 | C | - Light gray clay. Parent material is a till that breaks into blocky fragments. pH 7.6. |

PROFILE 3.

Profile 3 was sampled north-west of Buffalo Lake in S.E. 12-74-8-W6. This profile was taken in a valley in a well drained position.

Following is a description of Profile 3.

| Depth in inches | | |
|---|---|---|
| 0 - 3 | $A_1$ | - Very dark gray heavy loam practically structureless. pH 5.2. |
| 3 - 4 1/2 | $A_2$ | - Light brownish gray very fine sandy loam with a coarse platy structure. pH 5.8. |
| 4 1/2 - 5 | $B_1$ | - Light brownish gray clay loam. This horizon includes the round tops of the columns. pH 6.2. |
| 5 - 10 | $B_{21}$ | - Dark grayish brown clay. The hard compact columns are iron stained and root mats are promanent along the vertical cleavage lines. pH 7.2. |

Profile 3 (continued.)

| Depth in inches | | |
|---|---|---|
| 10 - 16 | $B_{22}$ - | Brown clay forming lower portions of columns. In this horizon there is less iron staining than in the one above. pH 7.4. |
| 16 - 18 | $B_{Ca}$ - | Light brownish gray clay with a nutty structure. pH 7.3. |
| 18 - 24 | $B_{SO_4}$ - | Light brownish gray clay with a granular and quite friable structure. Large accumulation of salts found in this horizon. pH 7.6. |
| 24 - 30 | $B_{SO_4}$ - | Light brownish gray granular clay with salts accumulations. pH 7.7. |
| 30 - 40 | C - | Light brownish gray clay to clay loam with a very fine granular structure. pH 7.8. |

## ANALYTICAL METHODS.

### Preparation of Sample.

After drying the samples the fines were separated out with a 2 mm. sieve and the remainder passed through a coarsely set hand grinder. Again the fines were separated and the larger lumps reground. The small particles were separated out after every grinding to prevent unnecessary breaking down of particles to sizes smaller than 2 mm. in diameter. In all about 5 or 6 grindings and separations were made before all the sample was put through a 2 mm. sieve. The products

of the repeated grindings were thoroughly mixed together and the sample stored in glass container.

Methods of Extracting.

Schollenberger and Dreibelbis (37) advocated the closed system for extracting the exchangeable bases. The advantage of such a system is that the chances of excessive evaporation and contamination from the outside are minimized. A simple apparatus was set up where the flask containing the leachate, the U-shaped funnel with the sample, and the flask collecting the extract were all connected up with tubing.

Another method tried was extracting the soil on a Buckner funnel as described by Bentley (4).

About six separate comparisons were made between the results obtained by the different methods. Comparison of total exchange capacity, and exchangeable hydrogen, calcium and magnesium showed no consistent or significant differences. However, extracting on a Buchner funnel was found to be much quicker and more practical. Though both systems can be used for intermittent leaching or extracting, the Buchner funnel and filter flask were found to be more suitable since suction can readily be applied when required. The use of the Buchner funnel method enables one to carry out the extracting on routine bases. About 16 samples can be extracted at a time and relatively little time and work is involved in setting up the apparatus. By using suction when necessary the time required for the extracting can be greatly reduced.

Ammonium Acetate Extracting Solution.

A 5N stock solution was prepared by dissolving 3,950 gms. ammonium acetate in 10 litres distilled water. This solution was then adjusted to pH 7.45 by using concentrated ammonium hydroxide and glacial acetic acid.

The required 1 N ammonium acetate extracting solution was prepared from the 5 N stock solution. Diluting of the stock solution resulted in the lowering of the pH. When required more ammonium hydroxide or acetic acid was used to adjust the reaction of the 1 N ammonium acetate to pH 7.05.

Extracting Procedure.

A 20 gm. soil sample was weighed out on a torsion balance and placed in a shaker bottle. Two 11 cm. filter papers and 50 ml. of 1 N ammonium acetate were added. The contents were placed in an over head shaker for two hours. The filter paper pulp, which was thoroughly mixed with the soil, made the sample much more permeable to the extracting solution.

For routine work 16 Buchner funnels and suction flasks were set up. Each funnel had a filter paper pulp mat covered by a sheet of filter paper. The contents of the shaker bottle were then transferred quantitatively to the Buchner funnel, evenly distributed and suction applied. The

sample was then leached with successive 50 ml. portions of leachate which were allowed to remain in contact with the sample for 5 minutes before aspiration. This intermittent leaching was continued till 450 to 500 ml. of extract was collected. This extract was saved for the determination of exchangeable hydrogen and bases.

The sample was then washed free of the excess ammonium acetate by using twelve to fifteen 10 ml. successive portions of 95% ethyl alcohol which had previously been tested for acidity as proposed by Peech (29).

Total Exchange Capacity.

To determine total exchange capacity the adsorbed ammonium ion was displaced by leaching the soil with successive 50 ml. portions of 1 N NaCl to a volume of 450 to 500 ml. An aliquot of the NaCl extract was placed in a Kjeldahl flask, concentrated NaOH added and the liberated ammonia caught in a standard acid.

For some of the soils the adsorbed ammonium ions were not displaced with another salt solution but the entire soil sample was placed in a Kjeldahl and some water, about 10 grams of NaCl, concentrated NaOH, and antifoam added. The ammonia was then distilled over into standard acid. This procedure was not very satisfactory because at times very large amounts of standard acid were required. Excessive foaming sometimes made distillation practically impossible.

Determining Exchangeable Hydrogen.

Exchangeable hydrogen was determined using a method similar to that given by Brown (6). Change in the pH of ammonium acetate extract was used as a measure of the amount of hydrogen extracted.

The extract was made up to a volume of 500 ml. with 1 N ammonium acetate, the pH measured by using a Beckman glass electrode pH meter and the exchangeable hydrogen was read off a curve.

The curve was obtained by titrating 500 ml. of 1 N ammonium acetate with .2 N acetic acid. By recording the pH at various intervals a graph was obtained. A representative curve is shown in Fig. 1.

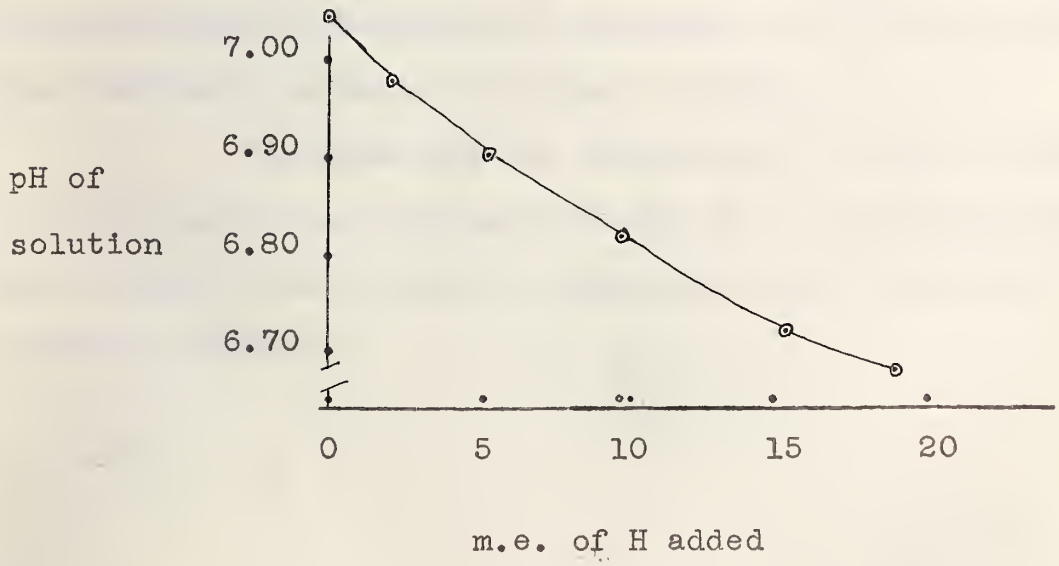



Fig. 1. Graph showing the decrease in pH of 500 ml. 1N ammonium acetate with the addition of $H^+$ as .2 N acetic acid.

The pH of the ammonium acetate extracting solution as measured with the potentiometer seemed to vary from day to day. To minimize error it was found necessary to make similar graphs each time a new set of exchangeable hydrogen determinations were made.

To test whether the change in pH of ammonium acetate extract was not affected by cations other than hydrogen, "sodium soil" and "calcium soil" were prepared.

Fifty grams of soil (Breton clay loam. Total exchange capacity 11.7 m.e. per 100 gms.) was left over night in contact with 50 ml. 1 N NaCl solution. This soil was then leached with 500 ml. of 1 N NaCl solution by using 50 ml. increments and suctions. The soil was washed with alcohol until it was free of chlorides. A "calcium soil" was similarly prepared by using 1 N $CaCl_2$.

Ten gram samples (replicated) of each of the prepared soils was leached with 250 ml. 1 N ammonium acetate and the pH of the solutions measured. The results are given in Table 1.

Table 1. Effect of exchangeable Ca and Na on the pH of 1 N ammonium acetate extract.

| | Original pH of ammonium acetate | pH of ammonium acetate extract |
|---|---|---|
| Soil in which the exchangeable cations are replaced with Na | 7.05 | 7.05 |
| | 7.05 | 7.07 |
| | 7.05 | 7.11 |
| | 7.05 | 7.08 |
| Soil in which the exchangeable cations are replaced with Ca | 7.05 | 7.05 |
| | 7.05 | 7.05 |
| | 7.05 | 7.05 |
| | 7.05 | 7.05 |

Calcium did not have any effect on the pH. In the case of the Na saturated soil there appeared to be a tendency of the pH to increase. However the increase was not any larger than difference that appeared in some duplicate determinations of exchangeable hydrogen in soils. This source of error was considered to be practically negligible.

However salts in the soil did appear to have an effect on the pH of the extract. In subsequent determinations it was noted that samples from the lower saline horizons usually increased the pH of the extract by about .3 units.

Preparation of Extract for Analysis of Bases.

The treatment of extract was essentially similar to that proposed by Peech (29). After exchangeable hydrogen was determined the extract was transferred to a 600 ml. beaker.

evaporated to dryness, and cooled. The residue was dissolved in 10 ml. concentrated $HNO_3$ and 2 ml. concentrated HCl. The contents were warmed gently, fumes allowed to subside, and then quantitatively transferred to a smaller (150 or 200 ml.) beaker. Again it was evaporated to dryness. The beakers were then placed into a muffle furnace, slowly heated to 390 $\pm$ 10° C and kept at that temperature for 15 minutes. After cooling, the residue again was dissolved in dilute HCl and evaporated to dryness to dehydrate silica. The beakers were removed, cooled, and the contents were immediately dissolved in 50 ml. .3 N $HNO_3$. Gentle heating helped dissolve the calcium sulfate. The contents were filtered and the beaker and filter paper washed with small increments of .3 N $HNO_3$ till the volume of the filtrate and washings was up to 100 ml. Aliquots of this solution which was the extract from 20 gms of soil, were taken for determination of sulfate, calcium and magnesium, sodium and potassium. Throughout the remainder of the report this solution is referred to as Solution A.

Determination of Sulfate

A 20 ml. aliquot of Solution A was used for determining sulfate gravimetrically by percipitating it as $BaSO_4$, filtering and igniting the filter paper.

Calcium and Magnesium Determination

Calcium and magnesium were determined on a 40 ml.

aliquot of Solution A. The solutions were first tested for sesquioxides and if necessary these elements were precipitated and separated by filtering of the hydroxides. Only in case of a few samples was there sufficient abundance of these elements in solution to form a precipitate that could be filtered off.

Calcium was then determined by precipitating as the oxalate and titrating with 0.1 N $KMnO_4$.

Magnesium was determined by evaporating the calcium oxalate filtrate to a small volume and percipitating the element as magnesium ammonium phosphate with microcosmic salt ($NaNH_4HPO_4$) solution and $NH_4OH$. The contents were allowed to stand over night in ammoniacal solution. The precipitate was then filtered, washed with 9% $NH_4OH$, air dried (over night), dissolved in standard $H_2SO_4$ and titrated with standard NaOH.

Determining pH of Soil

The pH of the soil was determined according to Doughty's (10) "thin paste" method.

Water Soluble Solids

A 1:5 soil to water ratio and Berkefeld filters were used for these determinations. An aliquot of the water extracted was evaporated to dryness and residue weighed.

For total solids determinations the residues

were dried at 110° C over-night. Non-volatile solids were determined after the residue was heated to 600° C and kept at that temperature for 20 minutes.

## Flame Photometer Method of Determining Exchangeable Potassium.

In recent years spectrophotometer methods of analysis have become increasingly common. Peech (29) outlined colormetric methods for determining magnesium, sodium, and potassium. Rogers (34) gave a method for these determinations using the spectrophotometer or flame photometer. For base exchange work he used buffered barium chloride as the extracting solution. Flame photometer techniques of determining exchangeable bases have been described by several workers (3,24,27,29,34,38). However, due to the difference of models of instruments, difference of materials to be analyzed, and difference of conditions under which the instruments are operated, it is necessary to work out a modified method to suit the particular condition. In soils that contain salts particular attention must be paid to the range and ratios of the cations that may occur.

In the method reported, it was found that in most cases Solution A was of proper dilution for the determination of potassium.

### Operation of the Instrument

The following setting of the flame photometer was

used for the determination of potassium.

| | |
|---|---|
| Wavelenghth | 769.9 mu. |
| Red-sensitive photo tube | |
| Slit width | .04 mm. |
| Oxygen pressure | 20 inches of water |
| Gas pressure | 2.5 cm. |
| Air pressure | 25 lbs. per sq. inch |
| Selector switch at | .1 position |
| Atomizer No. 1817H | |

In making the determinations the solutions were analyzed after calibrating the flame photometer against standard solutions of known potassium content. All of the stronger standards contained 100 p.p.m. of K plus varying amounts of Ca, Mg, and Na.

About three or four comparisons were made between each "unknown" and standard. Repeated readings of such comparisons did not vary more than two units on the transmission dial. Any greater variations were usually caused by noticeable change in air pressure, clogging of the atomizer, or by the effect of static on the galvanometer.

The effect of static on the galvanometer varied. Sometimes there was no interference while at other times it was so bad that it was impossible to get readings to agree within 10%. So far as the writer knows there is no remedy for static interference. When the interference was not too

bad it often decreased and disappeared when the instrument warmed up. At other times a copper wire connecting the phototube housing and shutter switch (where it also was in contact with the hand of the operator) to a ground, was found to be helpful.

By exercising special care and vigilance error due to changing pressure in gas, oxygen, or air can be considerably reduced. Frequent cleaning of the atomizer was necessary. Clogging of the atomizer could be detected when after a comparison of standard and unknown, the galvanometer needle failed to come back to its original position of 100% transmission when the standard was replaced. Blocking of the atomizer deflected the needle to the right. Avoiding unnecessary and excessive use of solutions greatly reduced the amount of atomizer trouble. It was found best to maintain the solutions under atomizer only long enough to make the required reading or adjustments, keeping at other times a beaker of distilled water under the atomizer.

In making determinations the following routine was used. Remove distilled water, place standard under atomizer, set transmission dial at 100, check dark current (with selector switch continually in .1 position), open shutter, zero the needle with the sensitivity knob, and close the shutter switch. Then place the unknown under the atomizer, check dark current, wait a few seconds, open shutter switch, zero the needle with the transmission knob, close the shutter

and note the dial reading. Replace unknown by distilled water to rinse out atomizer. Repeat this procedure a couple of times using the same standard and unknown until the readings are satisfactorily consistent.

Effect of Ca. Mg. & Na on K Determination

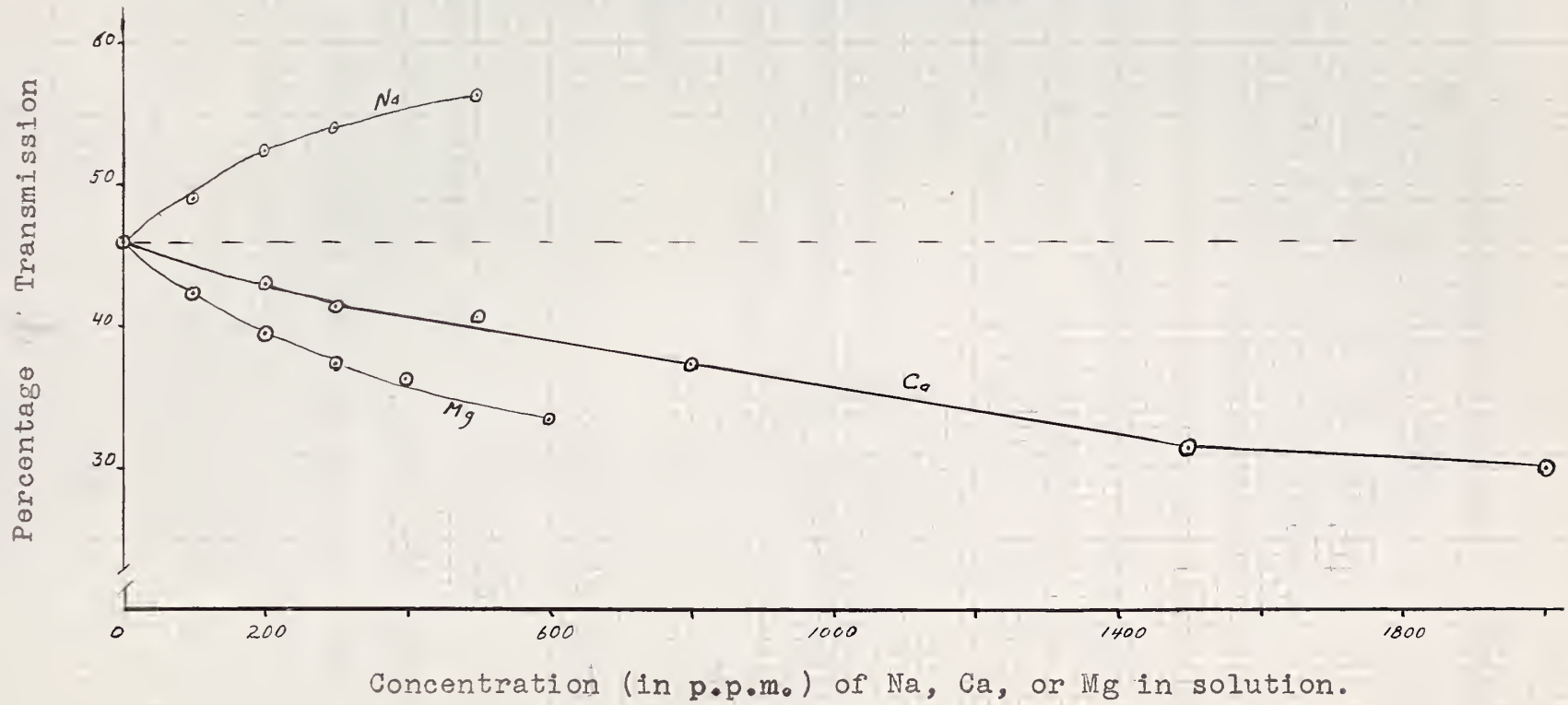
The interfering effects of certain ions in determination of K were reported by Attoe and Truog (3) and other workers. Before appropriate standards could be prepared it was necessary to determine the approximate effect of Ca, Mg, and Na on K determinations. Figure 2. shows a graph of the results obtained.

The standard used for obtaining these curves was 100 p.p.m. K as $KNO_3$ in .3 N $HNO_3$. The other solutions used consisted of a set of solutions containing 50 p.p.m. K as $KNO_3$ plus varying amounts of Ca as $CaCl_2$ in .3 N $HNO_3$. At least three comparisons, all of which agreed within 2 units, were made between each solution and the standard. The average transmission was graphed.

For lower concentrations of calcium, $CaSO_4 \cdot 2H_2O$ was also used but because of the low solubility of sulfate it was necessary to use the chloride to cover the enter range. The results plotted are those for the chloride but in the lower concentrations (up to 500 p.p.m.) the sulfate and chloride gave similar results.

Similarly using $Mg(NO_3)_2 \cdot 6H_2O$ and $NaNO_3$ graphs

Figure 2. Graphs showing the effects of addition of calcium, magnesium or sodium on percentage transmission of a potassium (50 p.p.m.) solution as measured by flame photometer.



showing the effect of Mg and Na respectively, were obtained.

Attoe and Truog (3) state that acids, bases and salts which increase surface tension of the solution give low readings and those which lower the surface tension give high readings. These workers who prepared solutions and standards using distilled water as a solvent found that HCl, NaOH, and $CaCl_2$ depress transmission readings. Using $KNO_3$ dissolved in .3N $HNO_3$ as standard, we obtained depressing effects from $Mg(NO_3)_2.6H_2O$ and $CaCl_2$ while the addition of $NaNO_3$ increased transmission.

The ranges of concentrations of each of the cations shown in Figure 2 corresponds to the ranges found in the extracts which were to be analyzed.

Preparation of Standards

The information from Figure 2 showing the effect of Na, Mg, and Ca on the percentage transmission reading for K was used as a guide to determine the kinds of standards to use. As previously stated errors of 2 units for repeated comparisons between an unknown and standard occurred. Levels of Ca, Mg, and Na in standards were so chosen that error due to these cations would not exceed 2%. The following levels of concentrations of the various cations were used.

| Na | Ca | Mg |
|---|---|---|
| 100 p.p.m. | 600 p.p.m. | 100 p.p.m. |
| 250 p.p.m. | 1000 p.p.m. | 300 p.p.m. |
| 500 p.p.m. | 1500 p.p.m. | 600 p.p.m. |
| | 2000 p.p.m. | |

The standards were always freshly prepared from concentrated stock solutions. The stock solutions were:

| | | |
|---|---|---|
| K | 1,000 p.p.m. K as $KNO_3$ | in .3N $HNO_3$ |
| Na | 1,000 p.p.m. Na as NaCl | " " " |
| Ca | 10,000 p.p.m. Ca as $CaCl_2$ | " " " |
| Mg | 10,000 p.p.m. Mg as $MgCl_2.6H_2O$ | in .3N $HNO_3$ |

All standards were made up by using the combination of cations which most closely resembled the concentration of the cations in the particular soil extract. Information from previous volumetric determinations was used as a guide to the selection of amounts of Ca and Mg included in the K standard solutions. The concentration of Na found in these soil extracts was approximated by using 100 p.p.m. Na standard and the flame photometer. This estimate was used to select the appropriate Na level for the K standard.

Using combinations of each of the cations at various levels of concentration, about a dozen standards were used to determine K in 35 samples from three soil profiles. It was later noted that for practical purposes the number of standards used could be substantially reduced without any great loss of accuracy.

Table 2 will give an idea of difference in results that may be expected due to differences in standard used. Five soil extracts were compared using four standards and the results

are expressed in p.p.m. as found in the solution and also as m.e. of exchangeable K per 100 gms of air-dry soil.

Table 2. Variation in amounts of potassium found in a soil extract due to the kind of standard used. (Results are expressed as p.p.m. K in solution and as m.e. of K per 100 gms. air-dry soil).

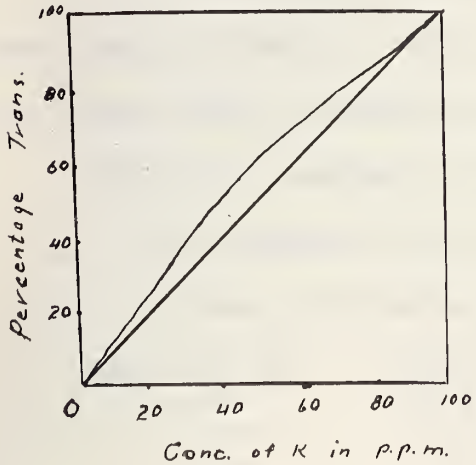
| | | Standard Used | | | |
|---|---|---|---|---|---|
| | | 1<br>100 ppm K | 2<br>100 ppm K<br>100 " Na<br>100 " Mg<br>600 " Ca | 3<br>100 ppm K<br>500 " Na<br>100 " Mg<br>1500 " Ca | 4<br>100 ppm K<br>250 " Na<br>100 " Mg<br>2000 " Ca |
| Soil Extract 1 - 1 | ppm K | 50 | 56 | 65 | 69 |
| | m.e. K | .64 | .72 | .83 | .88 |
| Soil Extract 2 - 2 | ppm K | 23 | 24 | 24 | 28 |
| | m.e. K | .29 | .31 | .31 | .36 |
| Soil Extract 1 - 9 | ppm K | 72 | 74 | 90 | 98 |
| | m.e. K | .92 | .95 | 1.15 | 1.25 |
| Soil Extract 2 - 4 | ppm K | 45 | 43 | 54 | 53 |
| | m.e. K | .57 | .55 | .69 | .68 |
| Soil Extract 2 - 5 | ppm K | 51 | 58 | 68 | 65 |
| | m.e. K | .65 | .74 | .87 | .83 |

It appears that in extreme cases the largest error

due to a poorly chosen standard would be about .3 m.e. per 100 gms soil. Duplicate determinations of potassium very often agreed within .01 m.e. per 100 gms of soil but sometimes differ up to .1 m.e. per 100 gms. In view of the fact that sometimes differences up to .1 m.e. may occur in duplicates one would appear to be justified in using only about half as many standards as were used in this work.

Potassium Standard Curves

A standard curve was prepared by using various concentrations of potassium. All of the stronger standards used contained 100 p.p.m. K plus varying levels of Ca, Mg, and Na. The shape of the curves obtained varied from practically a straight diagonal line as shown by Attoe and Truog (3) to a curve slightly concaved upwards as illustrated by Rogers (34). For concentrations of 100 to 0 p.p.m., the transmission ranged from 100% to practically 0. Also for the same standard the shape of the curve varied slightly from time to time. For this reason the curve was determined for the standard each day the determinations were made, by establishing five points on it i.e. 0 p.p.m., 25 p.p.m.,




Potassium Standard Curves.

50 p.p.m., 75 p.p.m., and 100 p.p.m. of K. Concentration of K in the unknowns were obtained by interpolating between these points.

In most cases Solution A (see page 21) was of proper dilution for determination of potassium.

Recovery Test for Potassium Determination

In order to test the method thus developed, a soil extract was taken and known increments of K were added. Then a potassium determination was made to see how much of the added potassium could be accounted for. The data ~~is~~ are given in Table 3. The extract used was from a sample from the $B_2$ horizon of Profile 2. All results are reported as p.p.m.

The solutions were made up by mixing 1 volume of soil extract with 1 volume of K solutions of the required strength.

Several other soil extracts were used and known amounts of K added. The recoveries of potassium were similar to those shown in Table 3.

Table 3. Amounts of potassium added to a soil extract and corresponding amounts of potassium found by using a flame photometer method of determination.

| Amounts of K added | Total Amount of K in sol'n. | Amount of the added K recovered. |
|---|---|---|
| 0 p.p.m. | 39 p.p.m. | -- |
| 5 " | 44 " | 5 p.p.m. |
| 10 " | 48 " | 9 " |
| 15 " | 52 " | 14 " |
| 20 " | 59 " | 19 " |
| 25 " | 62 " | 23 " |
| 37 1/2 | 75 " | 35 " |
| 50 " | 85 " | 45 " |

## Flame Photometer Method of Determining Exchangeable Sodium

An aliquot of Solution A was used for the Na determination. All the solutions and standards used were .3N with respect to $HNO_3$.

For sodium determination the following instrument setting was used.

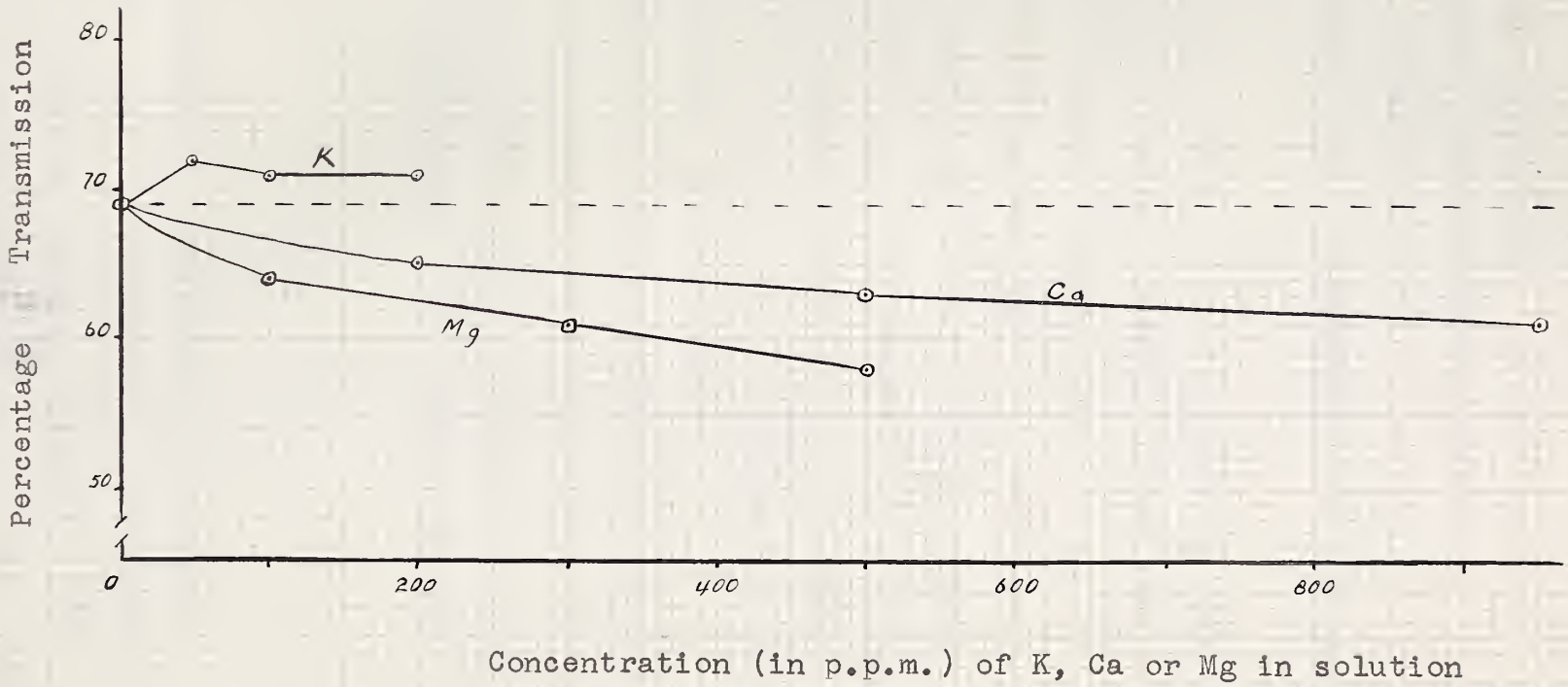
Wave length 589.6 mu.
Ultra-violet phototube
Slit-width .05 mm.
Oxygen pressure - 20 inches of water
Gas pressure - 2.5 cm.
Selector switch at .1 position
Atomizer number 1817 H.

The method of operating the instrument and the routine followed was similar to that outlined for the potassium determination. Sodium can be determined by using air pressures lower than 25 pounds per square inch but at lower pressures there appears to be a greater tendency for the atomizer to block. Also, at lower pressures the time lag between the time the solution is placed under the atomizer and the time the characteristic flame color appears, is slightly too long for routine work.

## The Effect of Ca, Mg, and K on Sodium Determination

The effects of various salts, acids, and bases

Figure 3. Graphs showing the effects of addition of calcium, magnesium or potassium on percentage transmission of a sodium solution as measured by flame photometer.



on flame photometer determinations have been shown and discussed by several workers (3,27,34,38). In this work an attempt was made to have the concentration and kinds of cation in the standards correspond fairly closely to those in the unknown. The solvent used for standards and unknowns was .3N $HNO_3$.

To estimate the extent of the interfering effect of Ca, Mg, and K on the determination of sodium three sets of solution were prepared and compared against 100 p.p.m. Na (as $NaNO_3$) standard. For the measurement of the effect of calcium, the solutions contained 50 p.p.m. Na plus varying amounts of calcium as $CaSO_4.2H_2O$. The magnesium solutions contained 50 p.p.m. Na and varying concentrations of Mg as $Mg(NO_3)_2.6H_2O$. The third set of solutions contained 50 p.p.m. Na and different concentrations of K as $KNO_3$.

Figure 3 shows the graphed results of these comparisons. The range of concentration of each of the mentioned cations is sufficient to cover the range that may be encountered in the soil extract when diluted down for the determination of sodium.

Standards

Using the graphed data in Figure 3 as a guide, standards were prepared so that the error due to difference in levels of Ca, Mg, and K would not exceed 2 percent. The following levels of concentrations of Ca, Mg, and K were used:

| Ca | Mg | K |
|---|---|---|
| 200 p.p.m. | 50 p.p.m. | 10 p.p.m. |
| 700 p.p.m. | 150 p.p.m. | 60 p.p.m. |
| | 350 p.p.m. | |

The standards were daily prepared from the following stock solution:

| | | | |
|---|---|---|---|
| Na | 1,000 p.p.m. | Na as NaCl in .3N $HNO_3$ |
| K | 1,000 " | K as $KNO_3$ " " " |
| Mg | 10,000 " | Mg as $MgCl_2.6H_2O$ in .3N $HNO_3$ |
| Ca | 10,000 " | Ca as $CaCl_2$ in .3N $HNO_3$ |

Using 100 p.p.m. Na as a standard the concentration of Na in the soil extract was estimated. This estimate of Na was used to determine the proper dilution to use. The concentration of Ca and Mg in the diluted soil extract was calculated from the results of volumetric analysis for those ions. Potassium concentration in the diluted extract was known from the flame photometer determinations. This information was then used to choose the appropriate level of the various cations to be used in the standard. The levels of concentrations of these cations in the standard were so chosen that they corresponded most closely to the concentrations in the unknown.

In the analysis of the three profiles about half a dozen standards had to be used. In view of the fact that standards were always prepared freshly from the stock solution, it was not found inconvenient to use this number of standards.

Unknowns that would require the same standard were grouped and determined at the same time.

The extent of the interfering effect of the other cations was fairly small. Determination on several soil extracts diluted down to proper concentrations were compared by using 100 p.p.m. Na as one standard, and then another standard contained the appropriate amounts of Ca, Mg and K. Differences in Na concentration obtained in the same solutions but due to differences in standards were up to 5 p.p.m. However this error when multiplied by the dilution factor (5 or 6) might become fairly significant in the final results.

A typical sodium standard curve is concaved upwards and the transmission range for concentrations of 100 to 0 p.p.m. Na is from 100% to practically 0. The standard used contained 100 p.p.m. Na plus the appropriate amounts of Ca, Mg, & K. The standard curves were recalibrated each day sodium determinations were made. This was done by establishing five points on the curve, i.e. 0 p.p.m., 25 ppm., 50 p.p.m., 75 p.p.m., and 100 p.p.m. of Na. The sodium concentration in the unknown was obtained by interpolating between these points.

Recovery of Sodium

The suitability of the procedure developed was tested in a fashion similar to that used for testing the potassium procedure. To a soil extract varying amounts of

sodium were added. Table 4 shows the results obtained for one soil extract.

Table 4. Amounts of sodium added to a soil extract and corresponding amounts of sodium found by using a flame photometer method of determination.

| Amount of Na added | Total Amount of Na in solution. | Amount of the added Na recovered |
|---|---|---|
| 0 p.p.m. | 41 p.p.m. | - p.p.m. |
| 5 " | 46 " | 5 " |
| 10 " | 50 " | 9 " |
| 15 " | 59 " | 18 " |
| 20 " | 62 " | 21 " |
| 25 " | 66 " | 25 " |
| 30 " | 75 " | 34 " |
| 40 " | 80 " | 39 " |
| 50 " | 90 " | 49 " |

A few single tests made on several other extracts gave equally good recovery.

Several days later another set of recovery tests on a different soil extract were made by using the same Na solutions. The results obtained were less consistent. This was probably due to change in concentration of the Na solution which were stored in pyrex erlenmeyers.

## RESULTS

The results given in this section are an average of at least duplicate determination which agreed within the following approximate limits:

(1) H - .5 m.e. per 100 gms air-dry soil

(2) Ca - .5 m.e. per 100 gms air-dry soil

(3) Mg - .2 m.e. per 100 gms air-dry soil

(4) Na - .05 m.e. per 100 gms air-dry soil

(5) K - .02 m.e. per 100 gms air-dry soil

(6) $SO_4^{=}$ - .2 m.e. per 100 gms air-dry soil

(7) Exchange capacity determined by $NH_4Ac$ method - .2 m.e. per 100 gms air-dry soil

(8) pH - .05 units.

In the lower horizons of the profile where large accumulations of salts were found, greater variations in duplicates (especially in calcium and sulphate determination) frequently had to be allowed. In the determination of total solids and non-volatile solids, the water extracts from the duplicates were filtered through the same Berkefeld filter and solutions were mixed. Duplicate determinations of the residues of the mixed solutions agreed within .01%.

TABLE 5. Profile 1 from Valleyview.

Amounts of cations extracted with 1 N ammonium acetate, water soluble solids (total and non-volatile), exchange capacity, and pH.

| Lab. No. | Depth in Inches | Horizon | Amounts extracted with $NH_4Ac$. in m.e./100 gms air-dry soil | | | | | | % Water Soluble Material | | * Exchange Capacity | | pH of Soil |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | H | Ca | Mg | Na | K | $SO_4^=$ | T.S. | n.v.s. | by $NH_4$ | by Sum | |
| 1-1 | 0-2 | $A_{11}$ | 17.7 | 17.2 | 3.6 | 2.6 | .75 | Nil | .20 | .10 | 33.8 | 41.9 | 5.6 |
| 1-2 | 2-5 | $A_{12}$ | 16.1 | 8.3 | 2.3 | 2.8 | .21 | Nil | .15 | .06 | 21.2 | 29.7 | 5.3 |
| 1-3 | 5-6 | $A_2$ | 13.6 | 8.8 | 2.3 | 3.1 | .33 | 1.6 | .16 | .08 | 18.4 | 26.5 | 5.2 |
| 1-4 | 6-8 | $B_1$ | 16.7 | 20.3 | 4.4 | 5.8 | .55 | 2.0 | .71 | .50 | 34.2 | 45.8 | 5.0 |
| 1-5 | 8-13 | $B_{21}$ | 12.2 | 31.7 | 6.0 | 6.9 | .50 | 1.8 | .36 | .16 | 46.6 | 55.5 | 6.1 |
| 1-6 | 13-20 | $B_{22}$ | Nil | 46.1 | 6.8 | 7.3 | .64 | 2.3 | .37 | .22 | 44.8 | 58.5 | 7.5 |
| 1-7 | 20-30 | $B_{Ca}$ | 2.7 | 42.8 | 6.1 | 7.3 | .90 | 9.3 | .53 | .46 | 41.0 | 50.5 | 7.4 |
| 1-8 | 30-36 | $B_{SO_4}$ | 4.1 | 49.5 | 5.8 | 7.9 | .85 | 20.5 | 1.16 | 1.05 | 38.6 | 47.7 | 7.3 |
| 1-9 | at 55" | C | Nil | 33.7 | 4.9 | 8.6 | 1.16 | 2.2 | .22 | .17 | 38.8 | 46.2 | 7.6 |
| 1-10 | 4 ft. | Bedrock | Nil | 26.4 | 3.6 | 7.5 | .82 | 3.0 | .18 | .16 | 19.8 | 35.3 | 7.5 |

* Expressed in m.e. as determined by ammonium acetate method and as the sum of the extracted cations less the $SO_4^=$.

TABLE 5A. Profile 1 from Valleyview.

Percentage of cations extracted from the various horizons with 1 N ammonium acetate.

| Lab. No. | Depth (inches) | Horizon | Percentage of Total Cations | | | | | pH of Soil |
|---|---|---|---|---|---|---|---|---|
| | | | H | Ca | Mg | Na | K | |
| 1-1 | 0 - 2 | $A_{11}$ | 42 | 41 | 9 | 6 | 2 | 5.6 |
| 1-2 | 2 - 5 | $A_{12}$ | 54 | 28 | 8 | 9 | 1 | 5.3 |
| 1-3 | 5 - 6 | $A_2$ | 48 | 31 | 8 | 11 | 1 | 5.2 |
| 1-4 | 6 - 8 | $B_1$ | 35 | 42 | 9 | 12 | 1 | 5.0 |
| 1-5 | 8 - 13 | $B_{21}$ | 21 | 55 | 10 | 12 | 1 | 6.1 |
| 1-6 | 13 - 20 | $B_{22}$ | 0 | 76 | 11 | 12 | 1 | 7.5 |
| 1-7 | 20 - 30 | $B_{Ca}$ | 5 | 72 | 10 | 12 | 2 | 7.4 |
| 1-8 | 30 - 36 | $B_{SO_4}$ | 6 | 73 | 9 | 12 | 1 | 7.3 |
| 1-9 | at 55" | C | 0 | 70 | 10 | 18 | 2 | 7.6 |
| 1-10 | 4 ft. | Bedrock | 0 | 69 | 9 | 20 | 2 | 7.5 |

TABLE 6. Profile 2 from east of Clairmont.

Amounts of cations extracted with 1 N ammonium acetate, water soluble solids (total and non-volatile), exchange capacity, and pH.

| Lab. No. | Depth in Inches | Horizon | Amounts extracted with $NH_4Ac$. in m.e./100 gms soil. | | | | | | % Water Soluble Material | | * Exchange Capacity | | pH of Soil |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | H | Ca | Mg | Na | K | $SO_4$ | T.S. | n.v.s. | by $NH_4$ | by Sum | |
| 2-1 | 0-2 | $A_1$ | 9.9 | 18.4 | 4.6 | 2.0 | .74 | -- | .20 | .04 | 41.4 | 35.6 | 5.5 |
| 2-2 | 2-4 | $A_2$ | 4.3 | 6.5 | 2.4 | 1.9 | .43 | 0.7 | .11 | .04 | 14.6 | 14.8 | 5.7 |
| 2-3 | 4-5 | $B_1$ | 3.5 | 12.6 | 6.0 | 5.1 | .37 | 0.6 | .26 | .14 | 26.8 | 27.0 | 5.7 |
| 2-4 | 5-10 | $B_{21}$ | 1.1 | 16.3 | 8.2 | 6.3 | .51 | 1.0 | .30 | .12 | 32.2 | 31.4 | 6.1 |
| 2-5 | 10-15 | $B_{22}$ | Nil | 33.4 | 12.5 | 8.8 | 1.04 | 1.8 | .29 | .14 | 40.2 | 53.9 | 7.5 |
| 2-6 | 15-21 | $B_{Ca}$ | Nil | 28.2 | 23.8 | 2.1 | .82 | 2.5 | .21 | .16 | 33.3 | 52.4 | 7.4 |
| 2-7 | 21-31 | $B_{SO_4}$ | Nil | 54.8 | 12.4 | 8.7 | .92 | 8.0 | .60 | .53 | 35.1 | 68.8 | 7.4 |
| 2-8 | 31-38 | C | Nil | 44.7 | 9.5 | 6.8 | .60 | 3.2 | .46 | .40 | 25.2 | 58.4 | 7.6 |

* Expressed in m.e. (per 100 gms. air-dry soil) as determined by $NH_4Ac$. method and as the sum of the extracted cations less the $SO_4^{=}$.

TABLE 6A. Profile 2 from east of Clairmont.

Percentage of cations extracted from the various horizons with 1 N ammonium acetate.

| Lab. No. | Depth (Inches) | Horizon | Percentage of Total Cations | | | | | pH of Soil |
|---|---|---|---|---|---|---|---|---|
| | | | H | Ca | Mg | Na | K | |
| 2-1 | 0-2 | $A_1$ | 28 | 52 | 13 | 6 | 2 | 5.5 |
| 2-2 | 2-4 | $A_2$ | 28 | 42 | 15 | 12 | 3 | 5.7 |
| 2-3 | 4-5 | $B_1$ | 13 | 46 | 22 | 18 | 1 | 5.7 |
| 2-4 | 5-10 | $B_{21}$ | 4 | 50 | 25 | 19 | 2 | 6.1 |
| 2-5 | 10-15 | $B_{22}$ | 0 | 60 | 22 | 16 | 2 | 7.5 |
| 2-6 | 15-21 | $B_{Ca}$ | 0 | 52 | 43 | 4 | 1 | 7.4 |
| 2-7 | 21-31 | $B_{SO_4}$ | 0 | 72 | 16 | 11 | 1 | 7.4 |
| 2-8 | 31-38 | C | 0 | 73 | 15 | 11 | 1 | 7.6 |

TABLE 7. Profile 3 from Buffalo Lake.

Amounts of cations extracted with 1 N ammonium acetate, water soluble solids (total and non-volatile), exchange capacity, and pH.

| Lab. No. | Depth in Inches | Horizon | Amounts extracted with $NH_4Ac$. in m.e./100 gms air-dry soil | | | | | | % Water Soluble Material | | *Exchange Capacity | | pH of Soil |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | H | Ca | Mg | Na | K | $SO_4$ | T.S. | n.v.s. | by $NH_4$ | by Sum | |
| 3-1 | 0-3 | $A_1$ | 20.1 | 21.2 | 11.0 | 1.9 | .66 | .4 | .26 | .06 | 51.7 | 54.5 | 5.2 |
| 3-2 | 3-4 1/2 | $A_2$ | 6.0 | 9.1 | 8.6 | 1.9 | .27 | .5 | .16 | .05 | 26.8 | 25.4 | 5.8 |
| 3-3 | 4 1/2-5 | $B_1$ | 5.2 | 6.0 | 8.4 | 2.6 | .26 | .6 | .20 | .08 | 16.2 | 21.9 | 6.2 |
| 3-4 | 5-10 | $B_{21}$ | 2.2 | 13.9 | 22.3 | 8.4 | .52 | .8 | .43 | .18 | 38.4 | 46.5 | 7.2 |
| 3-5 | 10-15 | $B_{22}$ | 0.2 | 13.0 | 23.8 | 10.6 | .53 | 3.8 | .40 | .24 | 37.3 | 44.3 | 7.4 |
| 3-6 | 16-18 | $B_{Ca}$ | Nil | 66.7 | 21.8 | 26.1 | .54 | 59.2 | 2.21 | 1.87 | 33.3 | 55.9 | 7.3 |
| 3-7 | 18-24 | $B_{SO_4}$ | Nil | 140 | 20.6 | 25.6 | .54 | 100.1 | 2.04 | 1.77 | 25.2 | 86.6 | 7.6 |
| 3-8 | 24-30 | $B_{SO_4}$ | Nil | 84.9 | 18.0 | 23.5 | .34 | 52.8 | 2.00 | 1.72 | 21.2 | 73.9 | 7.7 |
| 3-9 | 30-40 | C | Nil | 38.0 | 17.7 | 17.0 | .32 | 11.8 | .75 | .66 | 18.6 | 60.0 | 7.8 |

* Expressed in m.e. (per 100 gms. air-dry soil) as determined by $NH_4Ac$. method and as the sum of the extracted cations less the $SO_4^{=}$.

TABLE 7A. Profile 3 from Buffalo Lake.

Percentage of cations extracted from the various horizons with 1 N ammonium acetate.

| Lab No. | Depth (inches) | Horizon | Percentage of Total Cations H | Ca | Mg | Na | K | pH of Soil |
|---|---|---|---|---|---|---|---|---|
| 3-1 | 0-3 | $A_1$ | 37 | 39 | 20 | 3 | 1 | 5.2 |
| 3-2 | 3 - 4 1/2 | $A_2$ | 23 | 35 | 33 | 7 | 1 | 5.8 |
| 3-3 | 4 1/2 - 5 | $B_1$ | 23 | 27 | 37 | 12 | 1 | 6.2 |
| 3-4 | 5 - 10 | $B_{21}$ | 5 | 29 | 47 | 18 | 1 | 7.2 |
| 3-5 | 10 - 16 | $B_{22}$ | 0 | 27 | 49 | 22 | 1 | 7.4 |
| 3-6 | 16 - 18 | $B_{Ca}$ | 0 | 58 | 19 | 23 | 0 | 7.3 |
| 3-7 | 18 - 24 | $B_{SO_4}$ | 0 | 75 | 11 | 14 | 0 | 7.6 |
| 3-8 | 24 - 30 | $B_{SO_4}$ | 0 | 67 | 14 | 19 | 0 | 7.7 |
| 3-9 | 30 - 40 | C | 0 | 52 | 24 | 23 | 1 | 7.8 |

TABLE 8. Comparison of profiles with average (of 6) for the Black Zone. (Amounts extracted with ammonium acetate are compared with "Total Bases" as given by MacGregor and Wyatt (22).)

Solonetzic from Black Soil Zone

| Horizon | | m.e. of bases/100 gms air-dry soil | | | % of bases | | |
|---|---|---|---|---|---|---|---|
| | | Ca | Mg | Na | Ca | Mg | Na |
| $A_1$ | Average | 15.5 | 7.1 | 3.1 | 60 | 28 | 12 |
| | Range | 5.5-30.5 | 4.5-8.3 | .9-4.1 | 42-78 | 20-37 | 2-24 |
| $A_2$ | Average | 9.8 | 5.6 | 1.7 | 57 | 33 | 10 |
| | Range | 5.4-14.1 | 4.5-6.6 | 1.0-2.2 | 45-65 | 30-37 | 5-18 |
| $B_{21}$ | Average | 26.3 | 10.4 | 7.9 | 59 | 23 | 18 |
| | Range | 7.8-85.3 | 9.2-12.5 | 1.4-11.8 | 26-83 | 10-37 | 7-35 |
| $B_{22}$ | Average | 66.1 | 11.1 | 5.7 | 80 | 13 | 7 |
| | Range | 6.2-124.1 | 10.0-13.3 | 1.5-11.9 | 73-89 | 7-26 | 2-15 |
| Profile 1 | | | | | | | |
| $A_1$ | (Samples 1-1 and 1-2) | 12.8 | 2.9 | 2.7 | 70 | 16 | 15 |
| $A_2$ | (Sample 1-3) | 8.8 | 2.3 | 3.1 | 62 | 16 | 22 |
| $B_{21}$ | (Samples 1-4 and 1-5) | 28.4 | 5.5 | 5.9 | 71 | 14 | 15 |
| $B_{22}$ | (Sample 1-6) | 46.1 | 6.8 | 7.3 | 76 | 11 | 12 |
| C | (Sample 1-9) | 33.7 | 4.9 | 8.6 | 71 | 10 | 18 |
| Profile 2 | | | | | | | |
| $A_1$ | (Sample 2-1) | 18.4 | 4.6 | 2.0 | 74 | 18 | 8 |
| $A_2$ | (Sample 2-2) | 6.5 | 2.4 | 1.9 | 60 | 12 | 18 |
| $B_{21}$ | (Sample 2-3 and 2-4) | 15.7 | 7.8 | 6.1 | 53 | 27 | 20 |
| $B_{22}$ | (Sample 2-5) | 33.4 | 12.5 | 8.8 | 61 | 23 | 16 |
| C | (Sample 2-8) | 44.7 | 9.5 | 6.8 | 73 | 16 | 11 |
| Profile 3 | | | | | | | |
| $A_1$ | (Sample 3-1) | 21.2 | 11.0 | 1.9 | 62 | 32 | 6 |
| $A_2$ | (Sample 3-2) | 9.1 | 8.6 | 1.9 | 46 | 44 | 10 |
| $B_{21}$ | (Sample 3-4) | 13.9 | 22.3 | 8.4 | 31 | 50 | 19 |
| $B_{22}$ | (Sample 3-5) | 13.0 | 23.8 | 10.6 | 27 | 50 | 23 |
| C | (Sample 3-9) | 38.0 | 17.7 | 17.0 | 52 | 24 | 24 |

TABLE 8 (cont'd.)

Average of the 3 Profiles.

| Horizon | m.e. of bases / 100 gms air-dry soil | | | % of bases | | |
|---|---|---|---|---|---|---|
| | Ca | Mg | Na | Ca | Mg | Na |
| $A_1$ | 17.5 | 6.2 | 2.2 | 68 | 24 | 8 |
| $A_2$ | 8.1 | 4.4 | 2.3 | 55 | 30 | 15 |
| $B_{21}$ | 18.3 | 11.3 | 6.5 | 51 | 31 | 18 |
| $B_{22}$ | 25.1 | 12.9 | 8.1 | 54 | 28 | 17 |
| C | 38.8 | 10.7 | 10.8 | 64 | 18 | 18 |

## DISCUSSION OF RESULTS.

### Table 8.

This table was prepared for purposes of comparison of the three profiles with the solonetz of the Black Soil Zone reported by MacGregor and Wyatt. Amounts extracted with ammonium acetate are compared with "Total Bases" given by MacGregor and Wyatt. Soil samples used and compared were so grouped that the horizon used would correspond to the horizon report by MacGregor and Wyatt. Where an average of two soil samples was used, the relative depth represented by the samples was considered in making the estimate. Since MacGregor and Wyatt reported only on calcium, magnesium, and sodium content, the

amounts of these three major bases are compared and the results also expressed as percent of the sum of these cations. In addition to comparing the A and B horizons of these profiles with those of the Black Soil Zone, the parent material (C horizons) of the three profiles are also compared.

## Profile 1.

The following characteristics of Profile 1 should be noted:

(1) The A horizon and even the upper part of the B horizon in this profile are fairly acidic (Table 5 and 5A).

(2) Considering the analytical methods involved and the results obtained we can assume that cations extracted with ammonium acetate from the A horizon are predominantly exchangeable cations. However, in the lower horizons, due to the presence of soil salts, it is impossible to know what portions of the various extracted cations are exchangeable.

(3) This profile is similar to the average Black Soil Zone solonetz (22) in that calcium is the dominant cation but it differs in the sodium-magnesium ratio (Table 8). In this profile, especially in the $A_2$ horizon, sodium is relatively more abundant than magnesium. The percentage magnesium content of this soil approximately corresponds to the lowest percentage magnesium found in the six profiles reported on by MacGregor and Wyatt.

## Profile 2.

The following characteristics of Profile 2 should be noted:

(1) This soil contains appreciable amounts of exchangeable hydrogen in the upper horizons (Table 6 and 6A).

(2) In the A and $B_{21}$ horizons (Table 6 and 6A) the cations extracted with ammonium acetate, would appear to be predominantly exchangeable cations. In the lower horizons the extracted cations include exchangeable cations and cations from the soil salts.

(3) Of the three profiles studied, this one compares (Table 8) most closely to the solonetz found in the Black Soil Zone. Calcium is the dominant and sodium the least abundant of the extracted cations.

## Profile 3.

The following characteristics of Profile 3 should be noted:

(1) The A horizon of this soil has a fairly low pH and contains exchangeable hydrogen (Table 7 and 7A)

(2) Considering the results given in Table 7, it would appear that in horizons A and $B_1$ the extracted cations

are mostly exchangeable cations. Again, because of the soil salts it is not possible to tell what portion of the extracted cations in the lower horizons were displaced from the exchange complex.

(3) This profile differs from the average, as given by MacGregor and Wyatt (22) of the solonetz of the Black Soil Zone in that in the B horizon the Ca/Mg is less than unity. The relative amounts of the magnesium in this soil are generally larger than in any of the six solontzic profiles from the Black Soil Zone. With the predominance of magnesium this profile more closely resembles the solonetz reported on in Saskatchewan (5,25).

(4) This profile differs from Profiles 1 and 2 in that it contains more soil salts in the subsoil.

## General Discussion.

From Table 8 it may be noted that all three profiles are more similar to each other in percentage sodium than in the calcium-magnesium ratio. The average (of 3 profiles) percentage sodium in these soils is somewhat similar to the average of the Black Zone. The greatest difference is in the $B_{22}$ horizon.

The parent material would appear to contain a fair amount of salts (.2 - .6% non-volatile solids) and about 18% of the cations are sodium. The percentage of magnesium and calcium in the profiles is quite variable. The profiles

studied represent three levels of magnesium as expressed in percentage of total cations. In these three profiles there appears to be a positive correlation between the percentage magnesium in the parent material and percentage magnesium in the B horizon of the profile. This correlation seems to be in agreement with the data of Bentley and Rost (5) who report on Saskatchewan solonetz which contain a fairly large amount of magnesium in the parent material as well as in the B horizon.

The amount of potassium extracted with ammonium acetate is relatively small. On the average, potassium constitutes approximately 1% of the total extracted cations and the corresponding range is 0 - 3%. Though quantitatively potassium is relatively unimportant in base exchange studies of solonetz soils, determination of potassium gives an indication of the translocation of cations in the soil.

## SUMMARY

Solonetz soils of the Peace River District are morphologically similar to the solonetz reported elsewhere. Nevertheless chemical characteristics are quite variable and more studies and analysis are required before we can formulate definite conclusions.

On the basis of the work reported, it would appear that these solonetz soils are somewhat similar to the solonetz found in the Black Soil Zone. The low pH or the unsaturated exchange complex in the upper part of the solum is

common to the solonetz studied and those of the Black Soil Zone. Profiles 1 and 2 contain a predominance of calcium and in that respect are similar to the Black Zone solonetz. However, Profile 3 is more similar to the solonetz reported in Saskatchewan (5,25) in that magnesium is the dominant cation in the B horizon.

The parent material of the three profiles differed in the percentages of various extractable bases and this difference seemed to be further accentuated in the B horizon of the profile.

Flame photometer methods of determining exchangeable sodium and potassium were modified and tested. The methods, once modified and adapted for routine work, are relatively rapid and convenient.

## ACKNOWLEDGEMENT

Acknowledgement is due to:

Dr. J. D. Newton, head of Department of Soils, for making available the facilities of this department and for helpful suggestions and advice;

Dr. C. F. Bentley, Department of Soils, for all the helpful suggestions, advice, and criticism he gave throughout the course of this study;

Mr. W. Odynsky, Soil Survey, for assisting with the sampling and offering helpful advice;

The staff of the Soils Department for their co-operation and helpfulness during the course of this investigation;

Alberta Research Council for the financial assistance given in the final university year.

## BIBLIOGRAPHY

(1) Anderson, C.H. The determination of total magnesium in a sample of crushed wheat by means of the Beckman flame photometer. Soils 102 thesis, University of Alberta, 1949.

(2) Attoe, O.J. Rapid photometeric determination of potassium and sodium in plant tissue. Proc. Soil Sci. Soc. Amer. 12: 131-134. 1947.

(3) Attoe, O.J., and Truog, E. Rapid photometeric determination of exchangeable potassium and sodium. Proc. Soil Sci. Soc. Amer. 11: 221-226. 1947.

(4) Bentley, C.F. A study of some solonetz soil complexes in Saskatchewan. Doctor's thesis, University of Minnesota. 1945.

(5) Bentley, C.F., and Rost, C.O. A study of some solonetzic soil complexes in Saskatchewan. Soil Agric. 27: 293-313. 1947.

(6) Brown, Irvin. C. A rapid method of determining exchangeable hydrogen and total exchangeable bases of soils. Soil Sci. 56: 353-357. 1943.

(7) Chapman, H.D., and Kelly, W.P. The determination of the replaceable bases and the base exchange capacity of soils. Soil Sci. 30: 391-406. 1930.

(8) Collins, R.D. Using a flame photometer in determining potassium. Soils 102 assignment, University of Alberta. 1949.

(9) de Sigmond, A.A. The Principles of Soil Science. Thomas Murby & Company, London, 1939.

(10) Doughty, J.L. The advantages of a soil paste for routine pH determination. Sci. Agric. 22: 135-138. 1941.

(11) Ellis, J.H., and Caldwell, O.G. Magnesium clay solonetz. Trans. Third Intern. Cong. Soil Sci. 1: 348-350. 1935. (Frequently quoted by several writers (5.25,35).)

(12) Golden, L.B., Gammon, N., and Thomas, R.P. A comparison of methods of determining the exchangeable cations and the exchange capacity of Maryland soils. Proc. Soil Sci. Soc. Amer. 7: 154-161. 1942.

(13) Hanna, W.J., and Reed, J. Fielding. A comparison of ammonium acetate and buffered barium chloride methods of determining cation exchange properties of limed soils. Soil Sci. 66: 447-458. 1948.

(14) Hosking, J.S. The cation exchange capacity of soils and soil colloids. (Abstract) Soils and Fertilizers. 11: 369-370. 1948.

(15) Holowaychuk, N. Replaceable bases, hydrogen, and base holding capacity of Alberta soils. Master's thesis, University of Alberta. 1931.

(16) Hortie, H.J. The sodium content of oat straw as determined by the Beckman flame photometer. Soils 102 assignment, University of Alberta. 1949.

(17) Joffe, J.S., and Zimmerman, Miryam. Sodium, calcium and magnesium ratios in exchange complex. Proc. Soil Sci. Soc. Amer. 9: 51-55. 1944.

(18) Kelly, W.P. The so-called solonetz soils of California and their relation to alkali soils. Amer. Soil Survey Assoc. Bul. 15: 45-52. 1934. (Reference not seen. Frequently quoted by several writers (5,22,25).).

(19) Kellogg, C.E. Morphology and genesis of the solonetz soils of Western North Dakota. Soil Sci. 38: 483-500. 1934.

(20) Kjearsgaard, A.A. Determination of calcium in oat straw by flame photometer methods. Soils 102 assignment, University of Alberta. 1949.

(21) MacGregor, J.M. Studies on morphological solonetz soils of Alberta. Master's thesis, University of Alberta. 1938.

(22) MacGregor, J.M., and Wyatt, F.A. Studies on solonetz soils of Alberta. Soil Sci. 59: 419-435. 1945.

(23) Marshall, C.E. The use of membrane electrodes in the study of soils. Proc. Soil Sci. Soc. Amer. 7: 182-186. 1942.

(24) Mehlich, A. Determination of cations and anion exchange properties of soils. Soil Sci. 66: 429-445. 1948.

(25) Mitchell, J., and Riecken, F.F. The chemical nature of some typical soil profiles of Saskatchewan. Sci. Agric. 18: 109-119. 1937.

(26) Murphy, H.F., and Daniel, H.A. The chemical and physical properties of normal and solonetz soils and their relation to erosion. Soil Sci. 39: 453-461. 1935.

(27) Myers, Alfred T., Dyal, R. Stanley, and Borland, J.W. The flame photometer in soils and plant analysis. Proc. Soil Sci. Soc. Amer. 12: 127-130. 1947.

(28) Odynsky, W. Solonetz soils in Alberta. Sci. Agric. 25: 780-790. 1945.

(29) Peech, M. Determination of exchangeable cations and exchange capacity of soils - rapid micro-methods utilizing centrifuge and spectrophotometer. Soil Sci. 59: 25-38. 1945.

(30) Puri, Amar Nath. Electrofiltration. A new method of removing exchangeable basis from soil colloids. Soil Sci. 30: 413-419. 1930.

(31) Puri, Amar Nath. A new method of determining base exchange capacity of soils. Soil Sci. 37: 105-108. 1934.

(32) Puri, Amar Nath, and Uppal, H.L. A critical examination of the methods of finding base exchange capacity of soils. Soil Sci. 47: 245-253. 1939.

(33) Riecken, F.F. Some considerations in the magnesium cycle of weathering in solonetz soils. Proc. Soil Sci. Soc. Amer. 8: 391-395. 1943.

(34) Rogers, Lewis. Determination of exchangeable base with the air-acetylene flame and quartz photoelectric spectrophotometer. Proc. Soil Sci. Soc. Amer. 12: 124-126. 1947.

(35) Rost, C.O. Characteristics of some morphological solonetz soils of Minnesota. Jour. Amer. Soc. Agron. 28: 92-105. 1936.

(36) Salgado, M.L.M. A critical examination of analytical methods used in the determination of exchangeable potassium and sodium of soils. Soil Sci. 37: 39-48. 1934.

(37) Schollenberger, C.J., and Dreibelbis, F.R. Analytical methods in base exchange investigation on soils. Soil Sci. 30: 161-173. 1930.

(38) Toth, S.J., and Prince, A.L. Estimation of cations exchange capacity and exchangeable calcium, potassium, and sodium contents of soils by flame photometer techniques. Soil Sci. 67: 439-445. 1949.

B29760